Preface

The world of minerals with its diversity of forms, colors and properties is captivating. A mineral is formed as a result of natural, physical and chemical processes. Minerals are naturally occurring solid compounds having definite composition and physical properties. Minerals are highly complicated inorganic substances which cannot be understood even when its complete chemical analysis is available. As a result of the synthesis of large single crystals, minerals have become available for use as lasers, piezo crystals and probing devices in scintillators, ferromagnetic, Ferro elastics and acousto-optical instrumentation. This complexity of behavior in minerals and their synthetic analogues gives scope to employ different techniques such as optical absorption and Electron Paramagnetic Resonance to understand their behavior.

Nanotechnology is based on the fact that material properties are size dependent at nanoscale and is a result of substantial nanoscience that describes matter at quantum level. More precisely, it is a field of science that controls individual atoms, molecules in creating devices that are thousands of times smaller than current day products having more efficiency and low cost. The emergent field of nano-photonics deals more particularly with the interaction of optical fields with matter at nano regime. It creates a technological impact which perhaps cannot match up to any other technological developments that have taken place till date as it deals with every aspect of human life that ranges from building novel materials to medicine. Phosphors are the materials which convert absorbed energy into visible light without going to high temperatures, i.e. incandescence. They are also called as luminescent materials. A phosphor basically consists of host lattice in which activator ions are incorporated. The activator absorbs excitation energy and converts it into visible radiation. The structure of hosts, activator, impurity ions etc., influences the luminescent properties of lamp phosphors. Rare earth and transition metal ions which usually correspond to electronic transitions within the
incomplete 4f and 3d shell stimulate luminescence in phosphors resulting in narrow band spectra. The spectra, however is not dependent on the nature of host lattice. Materials which possess these characteristics are used in display systems. They also find application in light sources like fluorescent tubes, compact fluorescent lamps and cold cathode lamps, as diagnostic tool in medicine and biology.

Powder X-ray diffraction (XRD) is used to study the structural analysis of prepared phosphors. The surface morphology and elemental chemical composition is investigated by Scanning Electron Microscope (SEM) with Energy Dispersive X-ray Spectroscopy (EDS) analysis. Electron Paramagnetic Resonance (EPR) spectroscopy enables to identify the oxidation and spin states of transition metals as well as its binding site and symmetry. Optical absorption studies of materials give rise to ligand field absorption energies, which sensitively reflect the distortion of cubic, octahedral and tetrahedral coordination’s. It also provides the information about energy levels ordering, structure of complexes and the site symmetry of metal ion. Photoluminescence (PL) spectra can provide much information about the dopant atoms and it is an important tool to characterize the optical properties of phosphor materials. FT-IR spectroscopy is an important technique used to obtain information about the modes of vibrations of constituent elements in the prepared samples.

The aim of present thesis is to investigate transition metal ions bearing natural minerals (tennantite, chalcopyrite and rhodochrosite) and transition metal ions (VO(II), Co(II)) NaCaAlPO₄F₃ phosphor by using solid state reaction method to understand the nature of transition metal ions entered into host lattice, its site geometry, oxidation state, bonding nature and the luminescence studies are premeditated by using spectroscopic techniques. The results and discussions are presented in this thesis consists of *Seven Chapters* with brief summary and conclusion.
**Chapter 1** deals the brief introduction regarding mineralogy, natural minerals, nanotechnology, importance of nanophosphors, luminescence mechanism, history of phosphors and applications. About natural minerals (tennantite, chalcopyrite, rhodochrosite), preparations of present phosphor samples and basic features for the spectra of transition metal ions are also discussed. Various textbooks, monographs and research publications have been liberally referred in developing the subject matter of this chapter.

**Chapter 2** describes the basic theories and working principles of various experimental techniques which are used for the present investigation namely Powder XRD, SEM with EDS, UV-VIS-NIR absorption, EPR, PL and FT-IR spectrometers.

**Chapter 3** presents the spectroscopic characterization of tenantite natural mineral. The crystal system is indexed to cubic crystal system and the evaluated lattice cell parameter is $a = 10.2201 \, \text{Å}$. The average crystallite size is calculated using Scherrer’s formula as 34 nm. Optical absorption spectrum exhibited characteristic bands of Fe(III) and Cu(II) in tetrahedral site symmetry. In the case of Cu(II) ions it is further distortion tetragonally distorted tetrahedral. The crystal field and Racah parameters are evaluated for Fe(III) ions. Crystal field and tetragonal field parameters for Cu(II) ions are also evaluated. EPR spectra of RT & LNT shows the presence of both Fe(III) and Cu(II) ions in the mineral. FT-IR spectrum of tennantite mineral exhibited various characteristic vibrational bands of As-OH, S-O, C-O and hydroxyl ions.

These results are presented at National Conference on “A.P. Science Congress” on 18th – 20th November 2010, Jawaharlal Nehru Technological University, Hyderabad and some of the results are also presented at National Conference on “AP science congress”, on 14th – 16th November 2012, Acharya
Chapter 4 gives the results and analysis of chalcopyrite natural mineral. Chalcopyrite sample is belongs to tetragonal crystal system with standard diffraction data of JCPDS file no. 83-0983 and 65-4850 and the corresponding lattice cell parameter are evaluated as $a = 5.3044 \text{ Å}$ and $c = 10.3836 \text{ Å}$. The average crystallite size is estimated to be 57 nm, which is in the order of nanosize. The average strain and dislocation density of collected sample was calculated as $\varepsilon_{\text{str}} = 0.1643 \times 10^{-3}$ and $\delta = 0.0815 \times 10^{15}$ lines/m. Optical absorption spectrum suggests tetrahedral coordination for Fe(III) ions. In the case of Cu(II) the coordination site symmetry is octahedral. EPR spectrum of resonance signals were observed for Cu(II) and Fe(III) ions. In the case of Cu(II) ions the evaluated $g$ and $A$ values suggests the octahedral coordination, whereas in the case of Fe(III) ions it exhibited tetrahedral sites. Which is also supported from optical absorption studies. FT-IR spectrum of chalcopyrite mineral exhibited various vibrational bands characteristic of S-O, C-N and N-H groups.

These results are presented at National Seminar on “Development and Sustainability of Earth Resources and Environment” on 12th – 13th March 2011, Adikavi Nannaya University, Rajahmundry, A.P. These results are communicated to Radiation Effects and Defects in Solids (2014).

Chapter 5 contains the results and discussion of rhodochrosite natural mineral. From powder XRD pattern, the diffraction data is indexed to a rhombohedral crystal system and corresponding lattice cell parameter are evaluated as $a = 4.7806 \text{ Å}$ and $c = 15.7008 \text{ Å}$. The average crystallite size is evaluated as 57 nm. Microstrain and dislocation density are evaluated as $\varepsilon_{\text{str}} = 0.1760 \times 10^{-3}$ and $\delta = 0.0963 \times 10^{15}$ lines/m. Optical absorption spectrum exhibits six characteristic bands of Mn(II) ions with distorted octahedral site symmetry in
rhodochrosite mineral. A typical X-band EPR spectrum is observed at room temperature for rhodochrosite has broad line centered at $g = 2.0981$, characteristic of distorted octahedral site symmetry of Mn(II) ions. The hyperfine splitting ($A$) parameter is evaluated as $A = 123 \times 10^{-4} \text{ cm}^{-1}$. Which suggests Mn(II) in octahedral coordination. The bonding nature between Mn(II) ions and its carbonates is covalent. FT-IR spectrum exhibited various vibrational bands characteristic of C=O stretching vibration and carbonate bands.

These results are communicated to Spectrochimica Acta A (UK) (2014).

Chapter 6 elucidates the spectroscopic investigations of VO(II) ions doped NaCaAlPO$_4$F$_3$ phosphor was successfully synthesized by solid state reaction method using flux. Powder XRD studies reveal that the prepared phosphor belongs to monoclinic crystal system. The lattice cell parameters, microstrain and dislocation density are evaluated: $a = 0.6858$, $b = 0.7218$, $c = 0.5554$, $\beta = 108.98^\circ$; $0.198 \times 10^{-3}$ and $0.094 \times 10^{15}$ lines/m respectively. The size of the prepared sample is evaluated as 46 nm. From the results of optical absorption and EPR studies, the site symmetry of VO(II) ions are in octahedral coordination with tetragonal compression. The evaluated crystal field, tetragonal and spin Hamiltonian parameters supports the same. PL spectrum exhibited green, yellow and red emission peaks at excitation 420 nm and their corresponding CIE coordinates are in the yellowish green region at $(0.382, 0.509)$ which emphasize that prepared phosphor may be suitable for displays. FT-IR spectrum exhibited various vibrational bands characteristic of Phosphate, F-P, P-O-P and hydroxyl groups.

Chapter 7 discusses the results of Co(II) ions doped NaCaAlPO$_4$F$_3$ phosphor was synthesized successfully by solid-state reaction method. It was observed that the prepared phosphor belongs to monoclinic crystal system and the corresponding lattice cell parameters $a = 0.689$, $b = 0.718$, $c = 0.552$ nm and $\beta = 109.5^0$. The average crystallite size is calculated from Scherrer’s formula found to be 55 nm. Room temperature EPR spectrum showed broad resonance signal with effective g value $\approx 2.00$ which confirms the low spin Co(II) ions are in octahedral site symmetry. Optical absorption spectrum exhibited bands in visible and IR regions which are the characteristic of Co(II) ions in octahedral symmetry. PL spectrum exhibited UV and blue-green emission at excitation 285 nm and their corresponding CIE coordinates are in the blue region at $(x = 0.125, y = 0.129)$ which indicates that prepared phosphor may be suitable for UV LEDs and lamps. FT-IR spectrum exhibited various vibrational bands characteristic of Phosphate, F-P-F, P-O-P and hydroxyl groups.

These results are published as “Synthesis and Spectral Investigations of Co(II) Ions Doped NaCaAlPO$_4$F$_3$ Phosphor” in Proceedings of the National Seminar on Shaping the Future with Green Chemistry (SFGC-14), SPMH Kalasala, Machilipatnam, A.P. on 27$^{th}$-28$^{th}$ June 2014.